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# FINAL REPORT TO ONR

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## ABSTRACT

A detailed analysis of possible interfaces in cast aluminum silicon base reinforced particle composites containing SiC, Al<sub>2</sub>O<sub>3</sub> and C indicates that several different kinds of interfaces can form. The reinforcements may be totally surrounded by primary - phase, or primary silicon, or by the eutectic between Al and Si. In addition, in some cases, some of the original coatings or their reaction products in the case of coated particles (like nickel or nickel-aluminum intermetallics in nickel coated reinforcements, Cu or Cu- aluminum intermetallics in Cu coated reinforcements) may also form the interface. The reaction between dispersoids and the alloy itself can form a complex interface. These different interfaces have also been experimentally observed in the microstructures of cast particulate composites, with the exception of primary  $\alpha$ -aluminum surrounding the reinforcement.

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The absence of  $\alpha$ -aluminum on the reinforcements is attributed to possible lack of nucleation, persistent lateral growth and a thermal lag between the reinforcement and the matrix. Estimates of works of adhesion for the different interfaces observed in cast composites have been made using London Van der Waal equation, correlated to the properties of the composites, and used to identify the possibilities of further improving these properties.

## 1. Introduction

In the last few years considerable work has been done on the nature of simple interfaces in fiber reinforced metal matrix composites and their influence on mechanical properties. However relatively few attempts have been made to examine the nature of the interfaces which form in solidification processed metal matrix particulate reinforced composites, and their influence on the mechanical properties of particulate composites. Most of the time, the interface which is obtained as a consequence of solidification processing has been accepted as a fact accomplished, and hardly any attempts have been made to alter that interface and further improve the mechanical properties. This paper analyses the different types of interfaces which can form in Al-Si matrix particulate composites reinforced with SiC, Al<sub>2</sub>O<sub>3</sub> and graphite, and compares them with experimental observations in actual solidification processed composites. The paper discusses the influence of relative properties of interfaces like Aluminum-Silicon or Aluminum-Intermetallics which are present in the matrix, and the opportunities of improving the properties of these composites. Estimates of the matrix-reinforcement interfacial energies have been made, and the observed interfaces have been discussed in terms of heterogenous nucleation theory and the different interfacial energies in the solidifying composite. The possible correlations between the interfacial energies estimated

in this paper, the formation of interfaces during solidification processing, and the mechanical properties of these composites have been discussed, along with the opportunities to improve the properties of some of these composites.

### 1.1 Possible interfaces in cast particulate composites:

Generally the matrix systems in Aluminum base alloy cast particulate composites include, Al-Si, Al-Cu or Al-Zn-Mg alloys which have a eutectic type phase diagrams. The hypo eutectic, eutectic and hyper eutectic Al-Si base alloys are frequently used as matrices for particulate reinforcements including graphite, alumina and silicon carbide. The possible interfaces in these Al-Si matrix alloy systems can be between the primary  $\alpha$  aluminum and reinforcement, or between primary silicon and reinforcement, or between the eutectic of aluminum-silicon and the reinforcement. These possible interfaces are schematically shown in Fig.1. The interface between an eutectic of Al-Si and the reinforcement represents a complex bimaterial interface in which alternating platelets of eutectic aluminum and silicon are in contact with the reinforcement with a spacing of a few microns; the formation of such interfaces and their influence on the mechanical properties have not been studied. The size and spacing between eutectic Al and silicon will depend upon the solidification rate and will influence the properties of the composites. In addition to the interfaces with the reinforcement,

in Al-Si matrix composites, there are interfaces within the matrix region, including between  $\alpha$  Al and Si, and between  $\alpha$  aluminum or silicon and the intermetallic compounds or spinels which form in the matrix region and these will be discussed later.

An interface between primary  $\alpha$  - aluminum and reinforcement will be feasible when, nucleation of primary  $\alpha$  - phase occurs on a reinforcement particle, and its growth persists to encapsulate the reinforcement, as shown in Fig 2(a). Even when  $\alpha$  aluminium-phase nucleates away from reinforcements if the growing dendrites of  $\alpha$  - aluminum phase, entrap the reinforcement particles, as shown in Fig 2b, one can get an interface between the primary aluminium and the reinforcement. When the nucleation and growth of  $\alpha$  -aluminum phase does not occur on the reinforcement particles, or the particles are not entrapped by growing dendrites, one is not likely to observe the interface between primary  $\alpha$  - aluminum and the reinforcement particles. The ability to alter the solidification behaviour to create such an interface can change the properties of the composite.

The interface between primary silicon and the reinforcement particles will generally be observed when the matrix alloy is either hypereutectic to start with, or the liquid composition, locally near the particle shifts to hypereutectic composition possibly due to thermal lag between the particle and the matrix and due to concentration gradients. Either of these conditions



should be followed by the nucleation and lateral growth of primary silicon phase, encapsulating the reinforcement particle. The interface between the eutectic of  $\alpha$  -aluminum and silicon, and the reinforcement particle can occur, when primary  $\alpha$  - aluminum or primary silicon nucleates and grows away from the reinforcement particles, and the growing primary phases push the reinforcement into the interdendritic region; the composition of the liquid surrounding the particles shifts to eutectic or near eutectic composition which finally precipitates depositing alternating plates of eutectic  $\alpha$  - aluminum and silicon. If however, the liquid surrounding the reinforcement particles reaches a eutectic or near eutectic composition but solidifies in a divorced fashion, one can get either a continuous film of  $\alpha$  -aluminum or eutectic silicon around the reinforcements.

In addition to above mentioned interfaces, when the metal or ceramic coatings on the reinforcements remain intact then the interfaces generated would be between the coatings and the primary aluminum or primary silicon, or with the eutectic between -Al and Si. If the coatings dissolve, then the interface can be between the reaction products and the reinforcement, or between the reaction product and the matrix. For instance if nickel coated reinforcements are introduced into molten aluminum (a) The nickel coating can remain intact, creating an additional interface between the matrix and nickel while retaining the interface

between the nickel and the reinforcement (fig 3 a), (b) The Nickel coating can dissolve leading to the formation of  $\text{NiAl}_3$  or  $\text{Al-NiAl}_3$  eutectic which forms the interface with the reinforcement as well as with the matrix as illustrated in fig 3b. Likewise if copper coated reinforcements are brought in contact with molten Aluminum-Silicon alloys the copper coating can remain intact creating an interface between copper and the reinforcement, and another between the matrix aluminum and copper as shown in fig 3(c); Alternately the copper coating can dissolve leading to the formation of  $\text{CuAl}_2$  or  $\text{Al-CuAl}_2$  eutectic which forms interfaces with the reinforcements or with the matrix, or with both, as shown in fig 3d. In addition, some new interfaces can form when the reinforcement reacts with the matrix creating a reaction product. For instance  $\text{Al-Si}$  can react with  $\text{SiC}$  reinforcement to form  $\text{Al}_4\text{C}_3$ - $\text{SiC}$  interface and matrix - $\text{Al}_4\text{C}_3$  interfaces, in addition to  $\text{Al-SiC}$  matrix interface which is retained in areas where no reaction has occurred; such an interface represents a complex bimaterial surface.

In addition to the above interfaces which form near the particulate reinforcements, other interfaces can be present in the matrix of cast aluminum based composites. For instance, in  $\text{Al-Si}$  alloy matrix composites, there will be Aluminum -Silicon interfaces, and their properties relative to the interfaces with the reinforcement will influence the performance of the composite.

In addition there are secondary alloying elements and impurities present in commercial aluminum alloy matrices, and these form intermetallic compounds like  $\text{FeAl}_3$  or  $\text{Mg}_2\text{Si}$  or spinels; these lead to the formation of additional interfaces between  $\alpha$  aluminum and these intermetallic compounds, and sometimes between the intermetallic compounds or spinels and the reinforcements. The relative strengths and adhesion of these interfaces with the matrix or with the reinforcement will determine the properties of the composite. The properties of the interfaces, and therefore the composite, will also be a strong function of the specific crystallographic plane of the reinforcement in contact with specific crystallographic plane of the matrix [1]. In the case of Al-SiC interfaces the dependence of the interfacial binding energies on the crystal structure and the crystallographic plane of SiC have been discussed by earlier workers. Further, in the case of Al-SiC interfaces, the bonding between Al and SiC can be between the layers of silicon atoms or carbon atoms in SiC, and aluminum and this will further influence the properties.

### 1.2 Experimental observations on interfaces in cast composites:

A large number of possible interfaces that were described as possible in the earlier section, have indeed been experimentally observed in Aluminum -Silicon base particulate composites ,with the exception of continuous interfaces between the primary  $\alpha$  -

aluminum and the reinforcements which have not been observed to date. Generally if the matrix is hypoeutectic Al-Si alloy, the reinforcements are found to be segregated into the last freezing interdendritic regions\* and the primary aluminum dendrites (Fig.4) do not contain any reinforcements. The interface with reinforcements is generally a complex bimaterial interface with the eutectic between silicon and aluminum growing around the reinforcements. Segregation of reinforcements into last freezing liquid presumably occurs due to lack of nucleation and absence of persistent lateral growth of  $\alpha$  aluminum on SiC particles, and the subsequent pushing of the reinforcements by the growing aluminum dendrites which have nucleated in the regions of the liquid away from the reinforcements. This segregation of reinforcements in the interdendritic regions is a matter of concern since the cracks propagate preferentially through dendrite boundaries leading presumably to poor toughness values [2].

The presence of primary silicon around the reinforcements is observed much more frequently than that of  $\alpha$  aluminum as illustrated in Fig.5 which shows primary silicon particles around the graphite reinforcement [3,4]. Fig. 6 shows polyhedral silicon surrounding a short graphite fiber resulting in graphite - silicon interface. This has probably formed due to preferential nucleation and growth of silicon on graphite. It was mentioned in the earlier section that complex interfaces can also form if the reinforcements are coated with metals like nickel or copper, which

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\* This leads to segregation of reinforcements in interdendritic regions (Fig.4a). If  $\alpha$  aluminum is nucleated on reinforcements, a more uniform distribution of particles can be achieved in cast composites which may improve the mechanical properties.

may dissolve in the matrix and form intermetallics or may remain intact around the reinforcements . Fig. 7 shows a case where nickel coating is intact in several places around nickel coated graphite fibers. In other places , primary silicon and nickel aluminum intermetallic compounds are observed around the graphite forming complex interfaces as shown in fig 7(b). Fig 8 indicates a microstructure where Nickel coated silicon carbide particles have been infiltrated with molten aluminum under conditions where the nickel coating is intact and the interfaces present are between nickel and silicon carbide and aluminum matrix and nickel. Figure 9 indicates the nature of the interfaces after severe reaction has occurred between molten aluminum and platelet SiC . In certain regions Al-SiC interface is retained, whereas in other regions SiC-Al<sub>4</sub>C<sub>3</sub> and Al-Al<sub>4</sub>C<sub>3</sub> interfaces are generated. Recently Wang et al [5] have demonstrated that magnesium aluminate (spinel) forms at the reinforcement interface in the cast SiC particulate aluminum alloy composites.

It is apparent from these observations that several different types of interfaces, some of which are highly complex in nature can be formed during evolution of microstructures in cast composites. The nature of the interfaces which actually forms depends upon the relative interfacial energies, nucleation and growth of primary phases on reinforcement, and on solidification processing conditions. Preferential nucleation and persistent

lateral growth of the primary phases on the reinforcements seems to be a very important phenomenon influencing the interfaces which are finally observed. Table I summarizes the interfaces experimentally observed in several cast metal matrix particulate composites. It appears that primary  $\alpha$  aluminum from aluminum silicon alloys does not generally nucleate and persistently grow on the reinforcements. The assumption being made is that the experimental observation of an interface can be taken as an indication of nucleation and persistent lateral growth.

In the following section, nucleation probability of primary aluminum and primary silicon on silicon carbide, alumina reinforcements during solidification of Aluminum -Silicon base alloy matrix composites are analysed. In addition, the surface energies in these composites have been estimated using different methods. The possible influence of these energies on the formation of different interfaces and their influence on mechanical properties have been discussed.

## 2. Theoretical Considerations on Nucleation of Primary Aluminum and Silicon on Reinforcements.

During solidification of particulate composites, when the temperature of the melt-particle slurry is lowered below its liquidus temperature, the molten alloy becomes metastable with respect to formation of the primary phase. Classical nucleation

theory considers the minimum total free energy barrier along a path followed by the primary phase, when the size of its crystal increases [6]. The total free energy change for the solidification of a crystal of  $n$  atoms is

$$\Delta G = -n V_a \Delta G_v + M n^{2/3} \cdot \Delta \sigma$$

$$\text{where } \Delta \sigma = \sigma_{SL} + \sigma_{SP} - \sigma_{PL}$$

where  $V_a$  is the atomic volume of the solidifying phase,  $\Delta G$  is the change in chemical free energy per unit volume due to solidification of the primary phase,  $M$  is a geometrical factor and  $\Delta \sigma = \sigma_{SL} + \sigma_{SP} - \sigma_{PL}$  where  $\sigma$  is the interfacial energies between phases marked, S, P, and L respectively for the solidifying primary phase, reinforcement particle and the molten alloy. The minimum of total free energy given by equation (1) will correspond to a critical size nucleus of shape of minimum surface energy for a given volume. If the surface energy is independent of the orientation of the solidifying crystal, the shape of the crystal will be spherical, as it is presumed in spherical cap theory of heterogeneous nucleation [6]. If the surface energy of the solidifying phase is anisotropic, the minimum surface energy shape for a given crystal can be found out by Wulff construction [7] for homogeneous nucleation, and by Winterbottom construction [8] for heterogeneous nucleation on a substrate. The free energy barrier for nucleation and the shape of nuclei will depend on and the interface energies,  $\sigma_{SL}$ ,  $\sigma_{SP}$  and  $\sigma_{PL}$ . There are some data

reported in the literature on solid-liquid interface energies from undercooling measurements during homogeneous nucleation and Gibb's Thomson effect; or from dihedral angles measurements at grain boundary grooves and from sessile drop tests .However, there are hardly any measured values of solid - solid interface energies for ceramic-metal systems. There are a few studies including that of Pilliar and Nutting [9] where solid-solid interface energies have been measured in metal-alumina systems by a method which is the solid analogue of sessile drop method . Many doubts have been raised in the past about the validity of these experiments on grounds that the shape of the solid drop may not have attained equilibrium dictated by the surface forces due to its rigidity.. These doubts are further strengthened by the recent experiments of Kennetich and Raj [10] who observed a large deviation in contact angle of solid drops in the same system, indicating a lack of equilibrium. In spite of these limitations, the interfacial energies estimated on the basis of experiments carried out by Pilliar and Nutting [9] are the only measured interface energies now available.

The first step in analyzing formation of interfaces by heterogeneous nucleation should therefore start by examining the different methods of estimating solid - solid interface energies because direct reliable measurements are not available . The values of these solid-solid energies are not only important for the formation of the interfaces during solidification processing



but they also influence the properties of composites as will be discussed later.

## 2.1 Energies of Solid-Solid Interface.

Solid-Solid interface energies between the solidified phases and the ceramic reinforcements can be estimated indirectly using a number of methods. Three different empirical approaches have been examined here for estimating the values of solid - solid interface energies relevant to the formation of interfaces in cast composites of current interest.

### 2.1.1. Fracture Energy Approach [11]

This approach is based on the assumption that fracture energy of interfaces between the materials can be approximated by the work of adhesion,  $W_{ad}$ . The interfacial energy between the solid nucleating phase indicated by S, and the particulate reinforcement indicated by P, may be evaluated using the following equation:

$$\sigma_{sp} = \sigma_{sv} + \sigma_{pv} - W_{ad}$$

Since fracture energies are available for various metal-ceramic systems at room temperature, evaluation of  $W_{ad}$  and  $\sigma_{sp}$  subsequently should in principle be possible. However, the fracture energy approach does not take into account the energy for plastic deformation. Hence, the estimated values of solid - solid surface energies by this method cannot be accurate and may result in

higher values due to the energy contribution from the plastic deformation. Also suitable extrapolation methods to estimate fracture energy to elevated temperature are not available, and the results of calculations made using this approach will not be used further in this paper.

2.1.2. Equation of state approach [12] According to this approach, the interfacial energies of any three phases formed by solid particles and liquid, denoted by  $\sigma_{PV}$ ,  $\sigma_{SV}$  and  $\sigma_{PS}$  respectively, obey the following generic equation of state:

$$\sigma_{PS} = \frac{(\sqrt{\sigma_{PV}} - \sqrt{\sigma_{SV}})^2}{1 - K \sqrt{\sigma_{PV} \cdot \sigma_{SV}}}$$

where  $k$  is a constant.

It has been shown [12] that the above equation holds good reasonably well for organic liquids with  $k = 0.015$ . Table II shows the estimates of  $k$  for different metal ceramic systems on the basis of different solid-solid interfacial energies measured by Pilliar and Nutting [9]. On the basis of Table II, one may assume that  $k$  is of the order of  $1.0 \times 10^{-3} \text{ cm}^2 / \text{erg}$  for different metal-ceramic systems of interest. There are, however, difficulties associated with the equation of state approach, and the estimates of surface energies could be rather inaccurate even for low energy

substances. For instance, the adoption of equation of state approach to the system where  $\sigma_{pv}$  and  $\sigma_{sv}$  are very close, results in significant error of estimation as both  $\sigma_{sv}$  and  $\sigma_{pv}$  dominate the equation. For example in Si and SiC system if we assume  $\sigma_{pv}=1938$  ergs/cm<sup>2</sup> and  $\sigma_{sv}=1195.5$  ergs/cm<sup>2</sup>, the estimated value of  $\sigma_{sp}$ , using equation of state approach is -13.6, which is obviously in error. Similiar low values of estimation have been reported by Auborg. [13]. As pointed out by Auborg, Neumann's approach yields

$\sigma$ 's for naphthalene and biphinyl as 0.59 mJ/m<sup>2</sup> and 0.64 mJ /m<sup>2</sup> which is almost two orders of magnitude smaller than experimental values of 61+ 11 mJ/m<sup>2</sup> and 50+ 10 mJ/m<sup>2</sup> respectively. Nevertheless, the simplicity of the approach makes it particularly attractive, and according to Neumann [14], it should be explored for metallic systems. In view of the drawbacks of this approach London Van der wall relation was used to estimate the surface energies in the present case.

### 2.1.3. London-Van der Waal Relation [15]:

For those metal ceramic systems, where the estimate of interface energy by equation of state is not reasonable, it may be computed using the London -Van der Waal dispersion equation.

$$W_{ad} = 2 \phi (\sigma_{sv} \cdot \sigma_{pv})^{\frac{1}{2}}$$

where,  $\sigma_{SV}$  is interfacial energy between solid substrate and vapor, and  $\sigma_{PV}$  is the interfacial energy between the particle and vapor. On the basis of work of adhesion calculated by Pilliar and Nutting [9] in metal ceramic systems, the constant  $\phi$  has been estimated to be around 0.25. The surface energies of various systems of our interest such as Al-Al<sub>2</sub>O<sub>3</sub>, Al/SiC and Al-Si/SiC have been estimated using this approach, and are reported in the third column of Table III.

The solid -liquid surface energy of matrix alloys are frequently not available in the literature. Spaepen [16] has introduced a model relation which may be used as a basis for estimating the surface energies of the matrix alloys. Table III gives the estimated surface energies in Al-Si alloy systems using the Spaepen model. On the basis of a simple thermodynamic criterion, the nucleation of the primary phase S on the particulate reinforcement P in contact with the liquid l, may be energetically feasible if

$$\sigma_{PL} > \sigma_{PS}$$

This thermodynamic criterion may not be satisfied apriori in a given system. One may try to suitably engineer the interface so that the primary ductile phase is nucleated around the ceramic dispersoid and the debonding of the particle from the matrix may not immediately result in an unstable crack. There are two ways in

which the system may be modified so that the relationship in equation (5) may be satisfied. One approach is to enhance liquid-dispersoid interface energy by addition of suitable trace elements. The other approach will be to reduce the interface energy between the solidifying phase and the reinforcement by changing the nature of surface of the reinforcement with the aid of prior or in-situ coating, or selecting a particular crystallographic plane forming the surface of the reinforcement. It may also be possible to tailor the matrix alloy chemistry in such a way that it lowers the interface energy,  $\sigma_{ps}$ , without significantly altering the surface energy,  $\sigma_{pl}$  of the matrix alloy or if possible, even increasing it.

Figure 10 shows the estimated interfacial energies in a normalized plot of relevant interface energies for various systems; column 4 of Table IV lists the prediction of whether or not nucleation is feasible on the basis of equation (5). The fortyfive degree line from the origin in Fig. 10, has above it the region where nucleation on a given heterogeneous surface is thermodynamically feasible according to the criterion given in equation (5). The objective of the normalized plot is to further identify different regions distinguishable in the context of nucleation. The boundary 'ab' in Fig. 10 corresponds to nucleation wetting angle of zero when  $\sigma_{SL} = \sigma_{LP} = \sigma_{SP}$ . In the region above 'ab', marked region I in Fig. 10,  $\Delta\sigma$  in equation (1) will be negative and there will be no free energy barrier for

nucleation. Also, the equilibrium between the liquid phase, the nucleating phase and the heterogeneous surface of the particle will not be established, and a dynamic situation of spreading of the nucleating phase will prevail. The description of spherical cap model or its successor models based on Young - Dupre type of equation formulated for equilibrium of sessile drops will not apply. The nucleation wetting angle of one hundred and eighty degrees will correspond to the boundary line 'cd', in the region bounded by lines ab and cd (marked Region II in Fig. 10)

Young-Dupre type of equilibrium will be established between the liquid, the nucleating phase and the surface of the particle. The theories of heterogeneous nucleation formulated so far are applicable in this region. In the region below line cd, marked Region III in Fig. 10, there will be no equilibrium, and the solidifying phase will tend to form by homogeneous nucleation. Table 4 shows possible nucleation of different phases on various reinforcements. Even though barrierless nucleation has been predicted for both primary  $\alpha$  aluminum and silicon, experimental observation indicates that primary  $\alpha$  aluminum generally does not appear to nucleate on these reinforcements. This may be due to thermal lag between the reinforcements and the matrix. Solidification heat transfer models to predict the temperature distributions in the neighbourhood of a fiber[17], indicate that there is thermal lag between the fiber and the matrix. The degree of thermal lag is discussed elsewhere; the thermal lag can lead to the formation of nonequilibrium microstructures in the vicinity of

the reinforcements.

### 3. Interfacial Strength:

If the bond between the reinforcements and the matrix is weak, the debonding is likely to occur at the interface between the matrix and the reinforcements as shown schematically in fig 11(a). If the bond between the reinforcements and the matrix is strong, but the interfaces between metal matrix and other intermetallic compounds or spinels are weaker, then the debonding is likely to occur at the latter interfaces (Fig.11b). The overall strength of the composites therefore depends not only on the interaction between the reinforcements and the matrix, but also on the interfaces with other phases in the matrix which form during solidification. This underlines the care which should be exercised in selecting the matrix alloy, and the solidification processing parameters. Even though the different types of interfaces which occur in these composites, and their relative properties will influence the properties of the composites, there is very limited data on interfacial strengths since the measurements are difficult (18-20). Interfaces generally do not have finite dimensions to characterise them in terms of usual mechanical properties like yield strength and youngs modulus unless they are coated reinforcements. Fracture energy and shear strength may be more usual parameters for characterisation of interfaces. Energy required to fracture interfaces, thus creating

two new surfaces, can be expressed in terms of work of adhesion. It has been observed that work of adhesion can be related to shear strength of the interfaces [21]. In view of this, the work of adhesion for different interfaces has been estimated in the present paper.

Work of adhesion was calculated using London Van Der Waals equation;

$$W_{ad} = 2\phi(\sigma_{SV} \cdot \sigma_{PV})^{\frac{1}{2}}$$

Value of  $\phi$  is taken as 0.25 based on calculation presented earlier in the paper.

The surface energies  $\sigma_{SV}$  and  $\sigma_{PV}$  are calculated using the following equation.

$$\sigma_{SV} = 1.2 (\sigma_{LV})_m + 0.45 (T_m - T)$$

where m denotes values at the melting point.

The calculated values of surface energies and works of adhesion are given in Table V.

Interfaces can vary generally from  $\alpha$ -aluminum completely surrounding the reinforcements, or silicon phase completely surrounding the reinforcements, or varying percentages of two or three phases surrounding the particle as shown earlier. For



instance, when eutectic Al-Si surrounds the particle as shown earlier the percentage of aluminum and silicon in the eutectic surrounding the reinforcements will depend on the cooling rate, chemistry of the liquid and whether divorcement of eutectic occurs. In view of this, we calculate the work of adhesion for a range of interfaces with reinforcements where % Si range from 0 (only Al) to 100% (only Si). The variation in work of adhesion with increase in relative amounts of silicon surrounding the reinforcements is estimated using the rule of mixtures for Al-Si-SiC systems (Fig 12). Work of adhesion increases from 743 ergs/cm<sup>2</sup> to 760 ergs/cm<sup>2</sup> with an increase in the percentage of silicon phase; This may contribute in a limited way to the strengthening of the interface. Similar variation of work of adhesion with the fraction of Si around the reinforcement for Al-Si-Al<sub>2</sub>O<sub>3</sub> system is shown in Fig. 13. It appears that nucleation of silicon on reinforcement particles like silicon carbide or alumina will create a marginally stronger interface. However, it is to be noted that the work of adhesion of reinforcement-silicon interface regardless of the fraction of Si in Al-Si alloy-alumina particle composite is lower than that in the case of Al-Si alloy-SiC particle composite.

Since the estimates of work of adhesion between either aluminium or silicon with SiC appear to be greater than between aluminum-silicon in the Al-Si alloy-SiC composite, the properties

of the composite may not be strongly dependent on the properties of the matrix reinforcement interface. The probable weak bond between aluminum and silicon, and the effect of presence of Si on properties may be the reason for the low values of fracture toughness reported in the literature (Table VI). It is apparent from this table that the fracture toughness decreases from 25 to 16 MPa when silicon is present in the base alloy, and some of this decrease may be partly attributed to the possible weak interface between silicon and aluminum. As a contrast in the Al-Si-Al<sub>2</sub>O<sub>3</sub> system, the work of adhesion between primary aluminum and alumina is lower than that between aluminum and silicon, and it may be possible to improve the properties of Al-Si alloy-alumina composites by strengthening of the interfaces with the reinforcement.

When the particles are completely surrounded by eutectic, generally only about 12% of the matrix interface will be with silicon and, 88% will be with the primary aluminum phase. The estimated work of adhesion of such a bimaterial surface will be in the neighbourhood of 745 ergs/cm<sup>2</sup> as shown in Fig 12. The extent of the coverage of the reinforcement by the silicon may be increased by suitable modification of surface energies so that the potency of the reinforcements for heterogeneous nucleation of primary silicon increases or by changing the processing conditions in such a manner that the eutectic may get

progressively divorced depositing out silicon on the reinforcement. The bimaterial interface between the eutectic Al-Si and the reinforcement deserves further investigation. In recent work, J.Cornie [22] has demonstrated that when the size of phases and the spacing between them in bimaterial interfaces generated by overaging is of a critical magnitude, one can get significant increase in transverse properties of fiber composites; similar improvements may be possible in particulate composite if the size and spacing between eutectic Al and Si surrounding the reinforcement is controlled through solidification processing conditions.

#### 4. Summary and Conclusions

This study indicates that several interfaces of different kinds can form in aluminum silicon base reinforced composites. Possible interfaces in these composites can be between the primary -aluminum and reinforcement, or between primary silicon and reinforcement, or between the eutectic of -aluminum and silicon and reinforcement. In addition, a variety of other interfaces are likely to form if the reinforcements are coated, or if there is a chemical reaction between the reinforcements and the base alloy, or other intermetallics or spinels formed on or away from

reinforcements during solidification .The relative interfacial energies of the matrix -reinforcement interface compared to  $\alpha$  - Al- Si interfaces or  $\alpha$  -Al- Intermetallic compound interfaces within the matrix would influence the properties of the composite. Experimental observations confirm the occurrence of most of these possible interfaces except those where primary  $\alpha$  -aluminum surrounds the reinforcements . This has been attributed to the possible lack of nucleation and persistent lateral growth of primary  $\alpha$  -aluminum on these reinforcements. Analysis of heterogeneous nucleation on reinforcements like silicon carbide and alumina, using values of solidifying phase reinforcement interfacial energies calculated in this paper through different methods including the work of adhesion, suggest that it should have been possible to nucleate both  $\alpha$  aluminum or silicon on these reinforcements. The anomalous observations on the absence of primary  $\alpha$  - reinforcement interface could be due to thermal lag between the solidifying phase and the reinforcement during solidification. The estimation of work of adhesion at the matrix reinforcement interfaces made in this paper, and other estimates of relevant interfacial energies in these composites, suggest that with increases in the amounts of silicon phase around the reinforcements, the properties of the interface improve, and therefore the composites exhibit better properties. Our estimates of interfacial energies have also been correlated to prior observations on fracture behaviour of these composites.

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TABLE I  
PRIMARY PHASE NUCLEATION IN CAST METAL MATRIX COMPOSITES

Alloy System	Reinforcements	Primary Phase Nucleating on Reinforcements
1. Hypereutectic Al-Si alloy	Graphite, SiC, $Al_2O_3$	Primary silicon
2. Al-Mg	$Al_2O_3$	None
3. Al-Li	$Al_2O_3$	None
4. Al-Cu	SiC, Graphite, $Al_2O_3$	None
5. Al-Mg	Ni-coated Graphite	$Al_3Ni$
6. Cu-Sn	$TiB_2$ -coated C	Alpha aluminum
7. Mg-Al	SiC	None
8. Ti-Cu	C	None
9. Al-Ti-B	$TiAl_3$	Alpha aluminum
10. Al-Ti-B	$TiB_2$	None
11. Al-Ti-B	$AlB_2$	None

TABLE II  
ESTIMATION OF CONSTANT K IN EQUATION-OF-STATE APPROACH

System	$\sigma_{SV}$ ergs/cm <sup>2</sup>	$\sigma_{PV}$ ergs/cm <sup>2</sup>	$\sigma_{PS}$ ergs/cm <sup>2</sup>	k 10 <sup>-4</sup> cm <sup>2</sup> /ergs
Au/Al <sub>2</sub> O <sub>3</sub>	1400	840	1710	8.84
Ag/Al <sub>2</sub> O <sub>3</sub>	1100	840	1505	9.11
Cu/Al <sub>2</sub> O <sub>3</sub>	1780	840	2145	7.51
Ni/Al <sub>2</sub> O <sub>3</sub>	2280	840	2475	6.20
Fe/Al <sub>2</sub> O <sub>3</sub>	2100	840	2140	6.53

$$(a) \quad k = \frac{1}{\sqrt{\sigma_{PV} \cdot \sigma_{SV}}} \left[ 1 - \frac{(\sqrt{\sigma_{PV}} - \sqrt{\sigma_{SV}})^2}{PS} \right]$$



TABLE III  
ESTIMATED INTERFACE ENERGIES IN DIFFERENT METAL-CERAMIC  
SYSTEMS

Composite System (1)	$\sigma_{PL}$ ergs/cm <sup>2</sup> (2)	$\sigma_{SL}$ ergs/cm <sup>2</sup> (3)	$\sigma_{PS}$ ergs/cm <sup>2</sup> (4)	$\sigma_{PL}/\sigma_{SL}$ (5)	$\sigma_{PS}/\sigma_{SL}$ (6)
(1) Al/Al <sub>2</sub> O <sub>3</sub>	1692.8	1366.4	158	10.71	8.65
(2) Al/SiC	1700.0	1366.4	158	10.76	8.65
(3) Al-Si/SiC	1620.0	1534.4	1376.5	1.17	1.11
(4) Au/Al <sub>2</sub> O <sub>3</sub>	1660.0	1710.0	>132	12.58	12.95
(5) Ag/Al <sub>2</sub> O <sub>3</sub>	1345.0	1505.0	143	9.41	10.52
(6) Cu/Al <sub>2</sub> O <sub>3</sub>	2067.8	2145.0	>255	8.10	9.71
(7) Ni/Al <sub>2</sub> O <sub>3</sub>	2068.1	2475.0	200	10.36	10.73
(8) Fe/Al <sub>2</sub> O <sub>3</sub>	2301.0	2140.0	>204	11.28	10.69

TABLE IV  
PREDICTED AND OBSERVED NUCLEATION BEHAVIOR DURING  
SOLIDIFICATION OF PARTICLE LIQUID SLURRIES

Composite System	$\frac{\sigma_{PL}}{\sigma_{SL}}$	$\frac{\sigma_{PS}}{\sigma_{SL}}$	Should Nucleation Occur?
1. Al/Al <sub>2</sub> O <sub>3</sub>	10.71	8.65	Yes
2. Al/SiC	10.76	8.65	Yes
3. Al-Si/SiC	1.17	1.11	Yes
4. Au/Al <sub>2</sub> O <sub>3</sub>	12.58	12.95	No
5. Ag/Al <sub>2</sub> O <sub>3</sub>	9.41	10.52	No
6. Cu/Al <sub>2</sub> O <sub>3</sub>	10.34	10.73	No
7. Ni/Al <sub>2</sub> O <sub>3</sub>	8.11	9.71	Yes
8. Fe/Al <sub>2</sub> O <sub>3</sub>	11.18	10.69	Yes

TABLE V

ESTIMATED VALUES OF SURFACE ENERGY AND WORK OF ADHESION  
IN ALUMINIUM Si-REINFORCED COMPOSITE

Phases	$\sigma$ , ergs/cm <sup>2</sup>	Wad, ergs/cm <sup>2</sup>	
SiC	1138.0	Si / SiC	761.07
Si	1195	Al / Al <sub>2</sub> O <sub>3</sub>	489.0
Al <sub>2</sub> O <sub>3</sub>	840	Si / Al	583.7
Al	1140	Al / SiC	743.28

Table VI. FRACTURE TOUGHNESS OF SELECTED COMPOSITES

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Base alloy	Dispersoid, Vol %		KQ, MPa M	Remarks
2080 (ALCOA)	SiC	15	25.2	
		20	24.0	
6xx1 (ALCOA)	SiC	15	49.2	Such improvement in KQ may not have been possible if SiC interface has been weak
		20	46.3	
A357 (DURAL)	SiC	15	16.5	Lower KQ--Possibly due to weak Al-Si interface?
2014  (Lanxide)	Al <sub>2</sub> O <sub>3</sub>	2	16.5	Does it indicate a weak Al <sub>2</sub> O <sub>3</sub> interface?
		5	15.8	
		20	12.	
		≥50	10-12	

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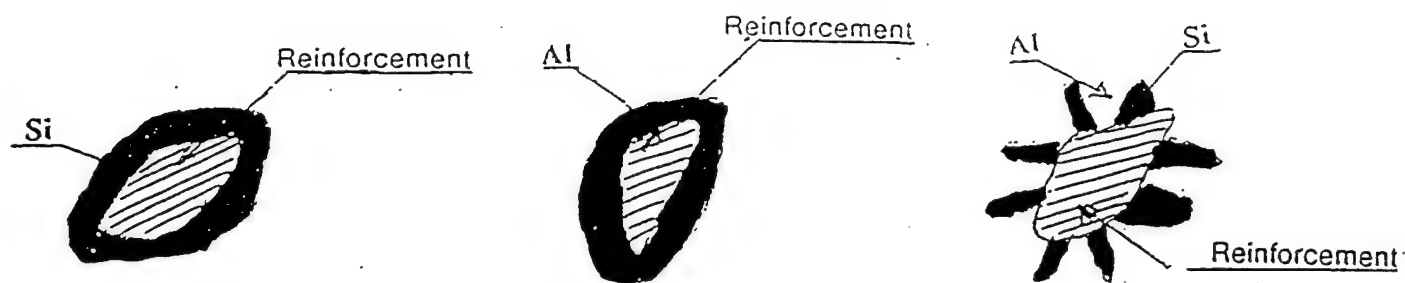


FIG 1. SCHEMATIC DIAGRAM SHOWING DIFFERENT POSSIBILITIES OF INTERFACES IN ALUMINIUM ALLOY PARTICULATE COMPOSITES.

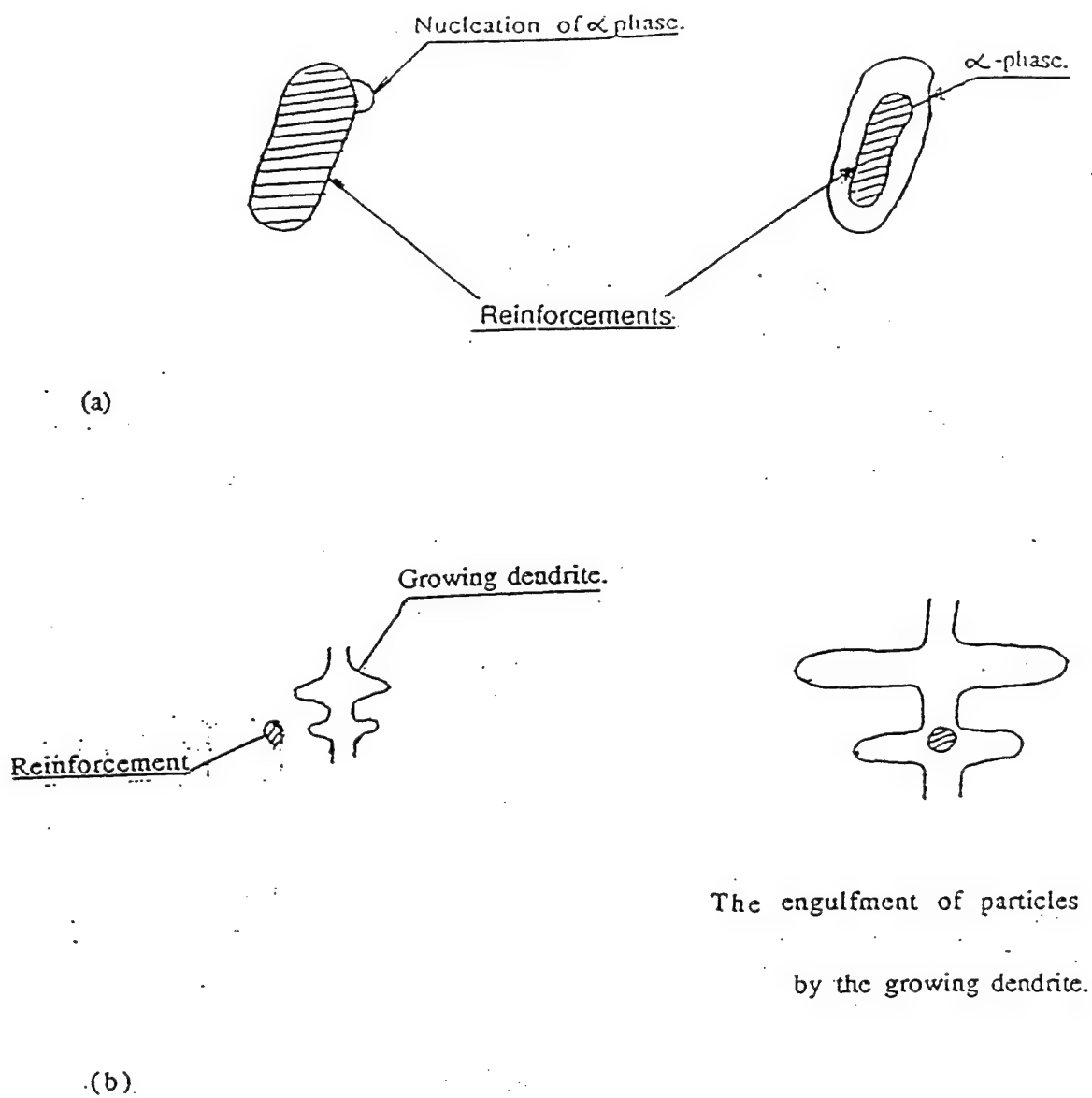


FIG 2.

SCHEMATIC ILLUSTRATION OF ENGULFMENT OF PARTICLES BY THE PRIMARY PHASE EITHER DUE TO NUCLEATION OR DUE TO CAPTURING OF PARTICLES BY GROWING DENDRITES.

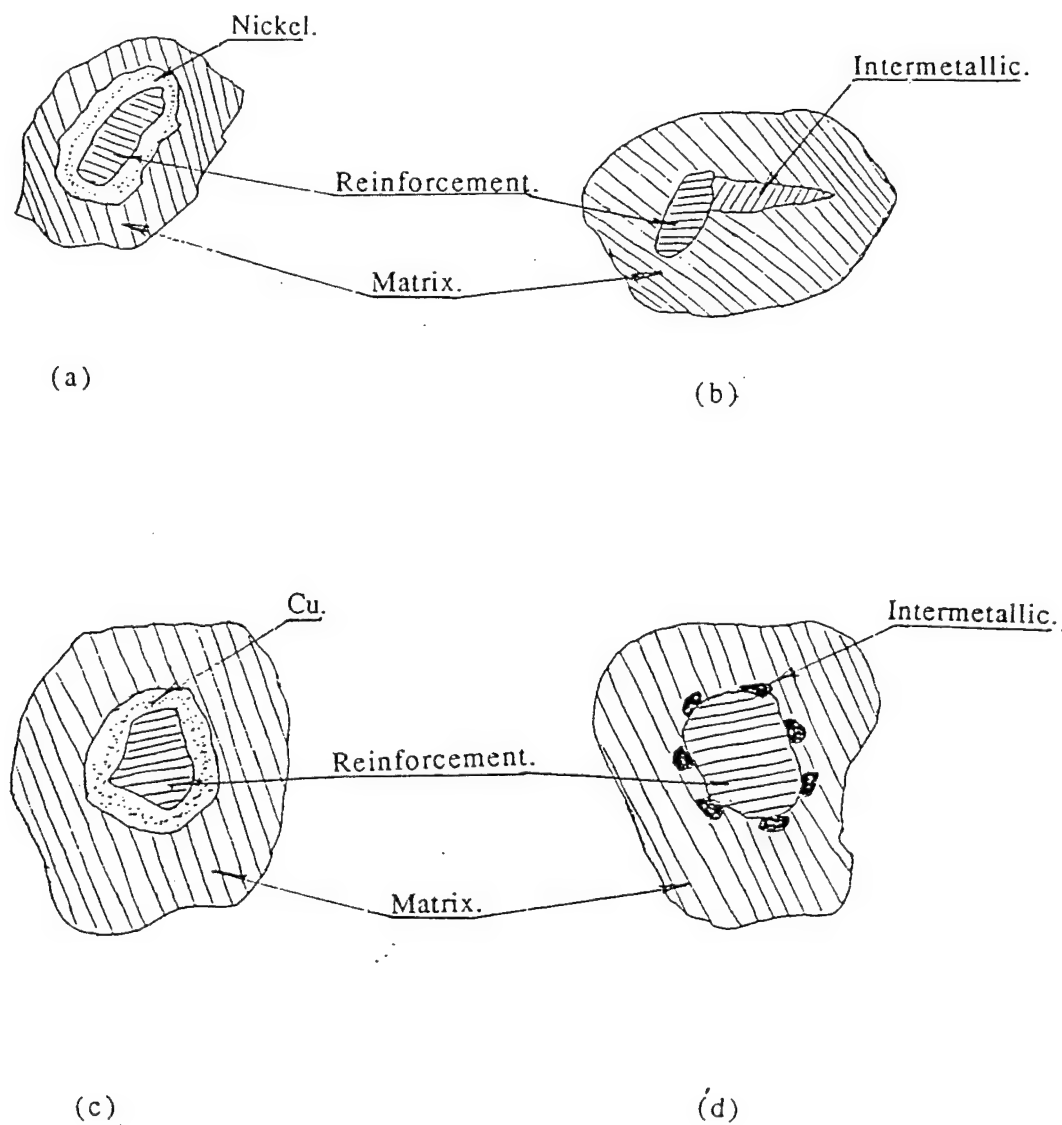
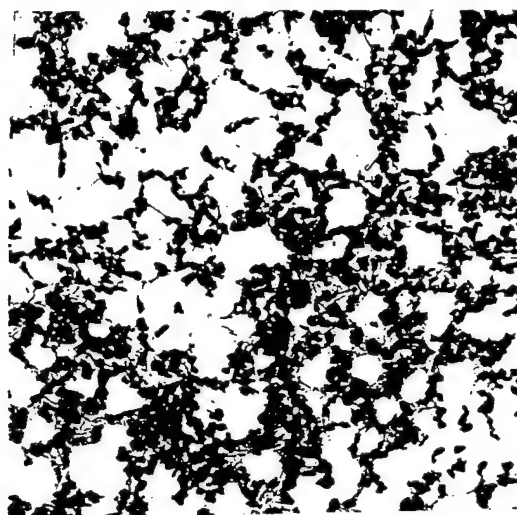


FIG 3. SCHEMATIC ILLUSTRATION OF VARIOUS KINDS OF INTERFACES THAT FORMS IN COATED REINFORCEMENTS.



(a) Al-Si-SiC Composite. Mag. 100X



(b) Al-Si-C Composite

FIG 4.

MICROSTRUCTURES SHOWING THAT DISPERSOIDS ARE IN THE  
LAST FREEZING LIQUID AND EUTECTIC GROWING ON THE  
DISPERSOIDS.





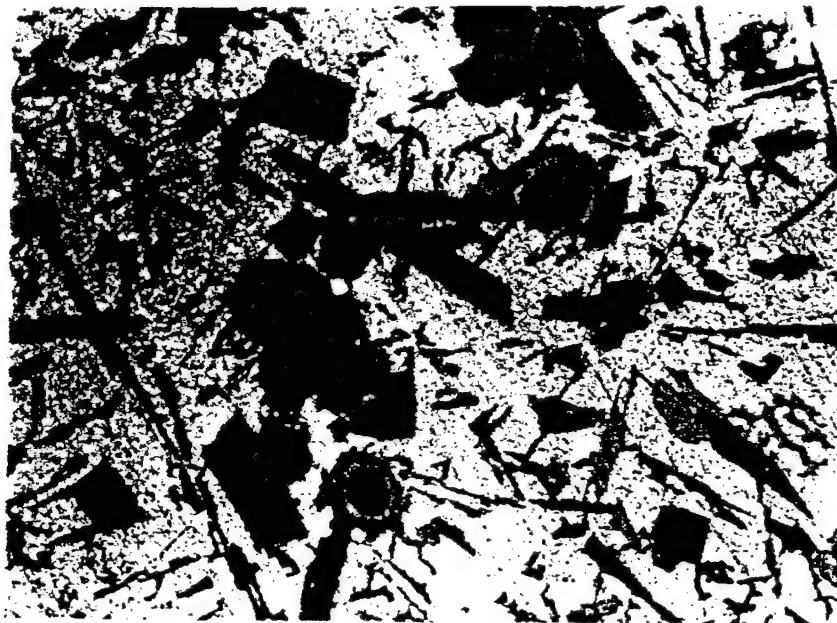
FIG 5. NUCLEATION OF SILICON PHASE ON GRAPHITE PARTICLE IN ALUMINUM SILICON - GRAPHITE COMPOSITE. MAG 440X.



FIG 6. NUCLEATION OF POLYHEDRAL SILICON AROUND THE GRAPHITE FIBER IN SQUEEZE PRESSURE INFILTRATED Al-Si-Ni COATED GRAPHITE COMPOSITE. MAG 440X.



FIG 7(a) SQUEEZE PRESSURE INFILTRATED Al-Si-Ni COATED GRAPHITE COMPOSITE ILLUSTRATING NICKEL INTERFACE BETWEEN MATRIX AND THE FIBER. MAG 440X.



7(b) SQUEEZE PRESSURE INFILTRATED Al-Si-Ni COATED GRAPHITE COMPOSITE SHOWING VARIOUS INTERFACES FORMED DUE TO REACTION. MAG 440X.

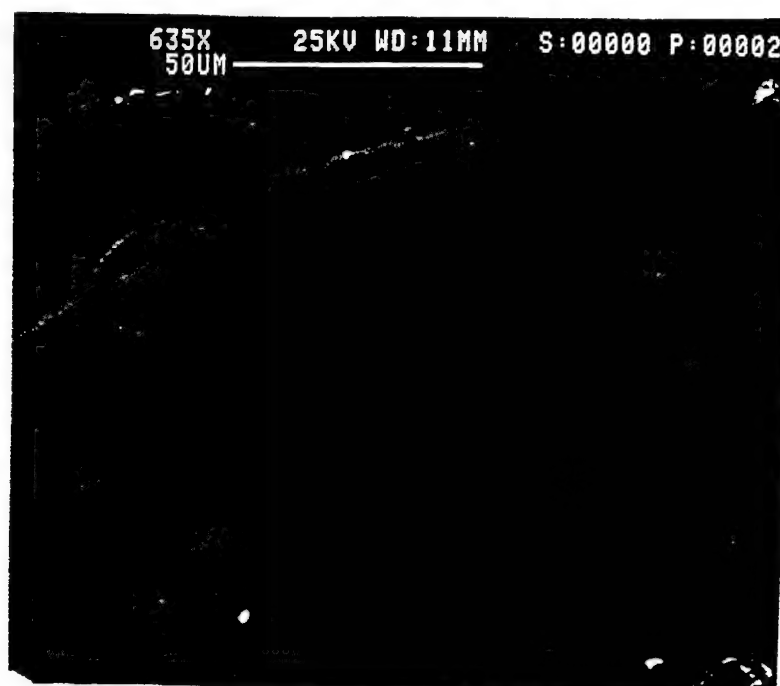


FIG 8.

NI COATED SiC INFILTRATED WITH ALUMINUM  
ILLUSTRATING THAT INTERFACES CONTAIN UNDISSOLVED  
NICKEL AROUND THE PARTICLES.

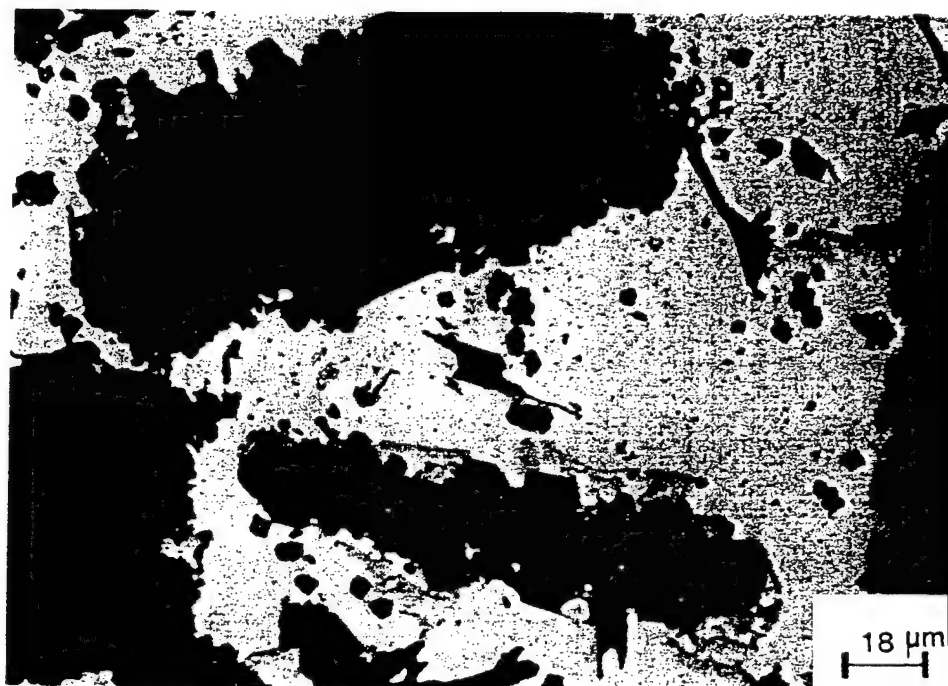


FIG 9. PHOTOMICROGRAPH SHOWING FORMATION OF A REACTION PRODUCT AT SiC SURFACE IN Al-Si-SiC COMPOSITE.

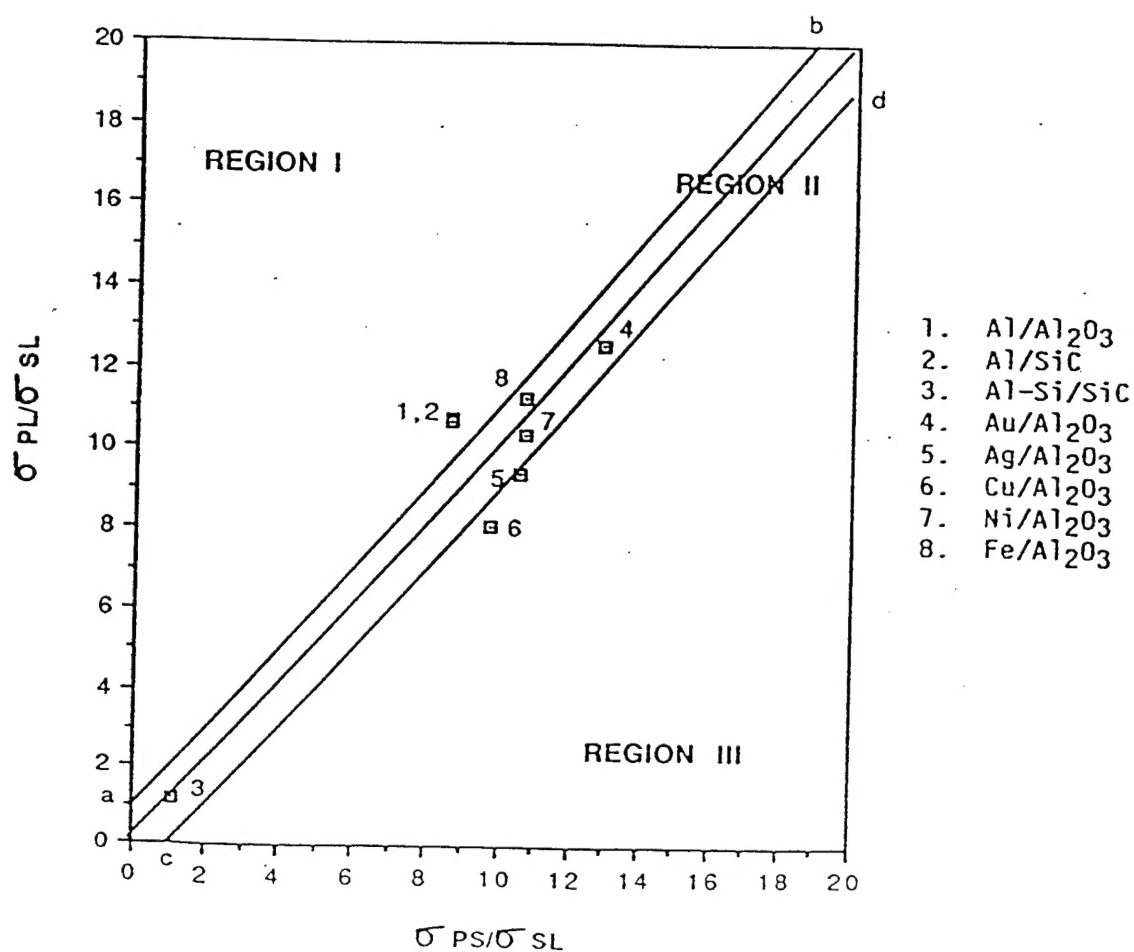


FIG 10. NORMALISED SURFACE ENERGY RELATIONSHIP TO DETERMINE NUCLEATION BEHAVIOUR.

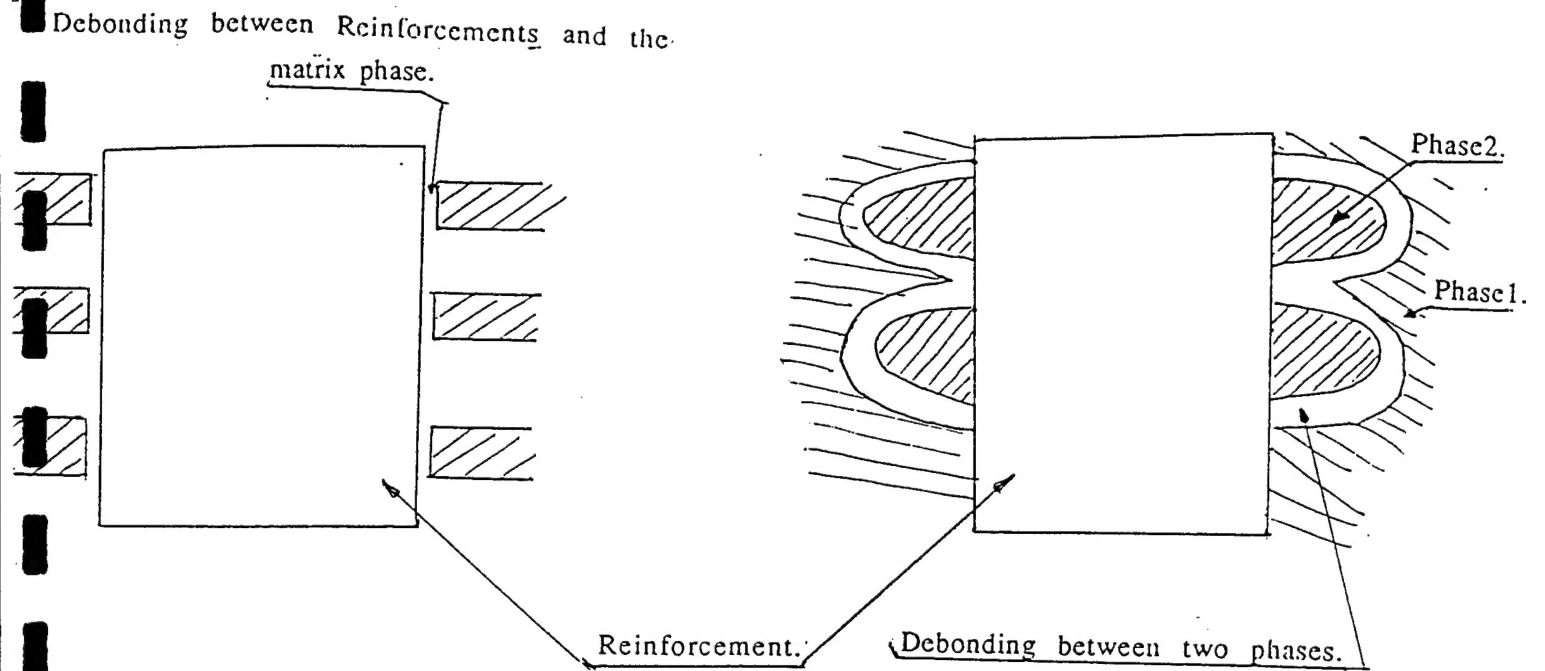


FIG 11. SCHEMATIC DIAGRAM SHOWING THE DEBONDING OF INTERFACES IN MMCS.

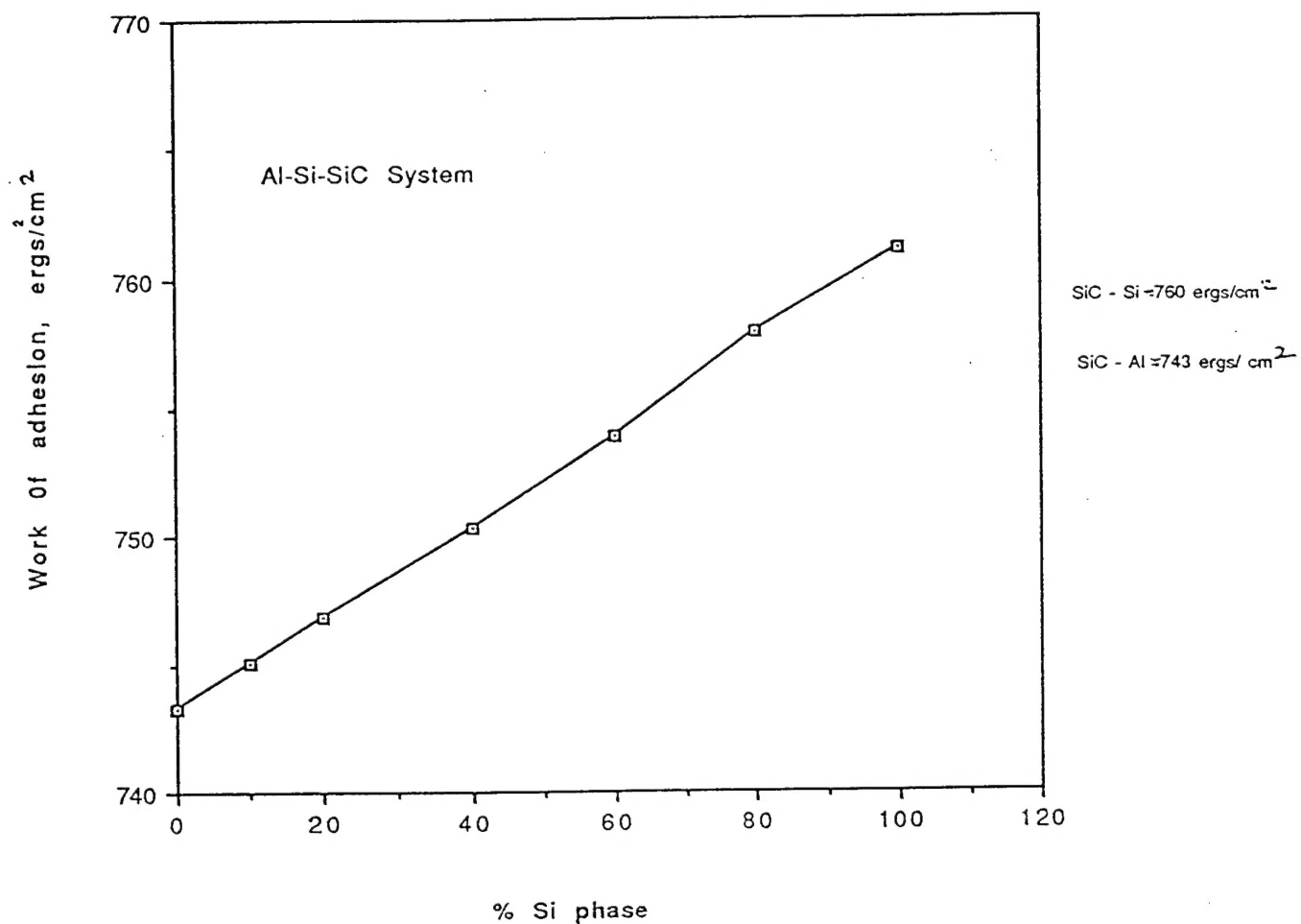


FIG 12

VARIATION IN WORK ADHESION WITH INCREASE IN VOLUME PERCENT OF SILICON PHASE AT THE INTERFACE



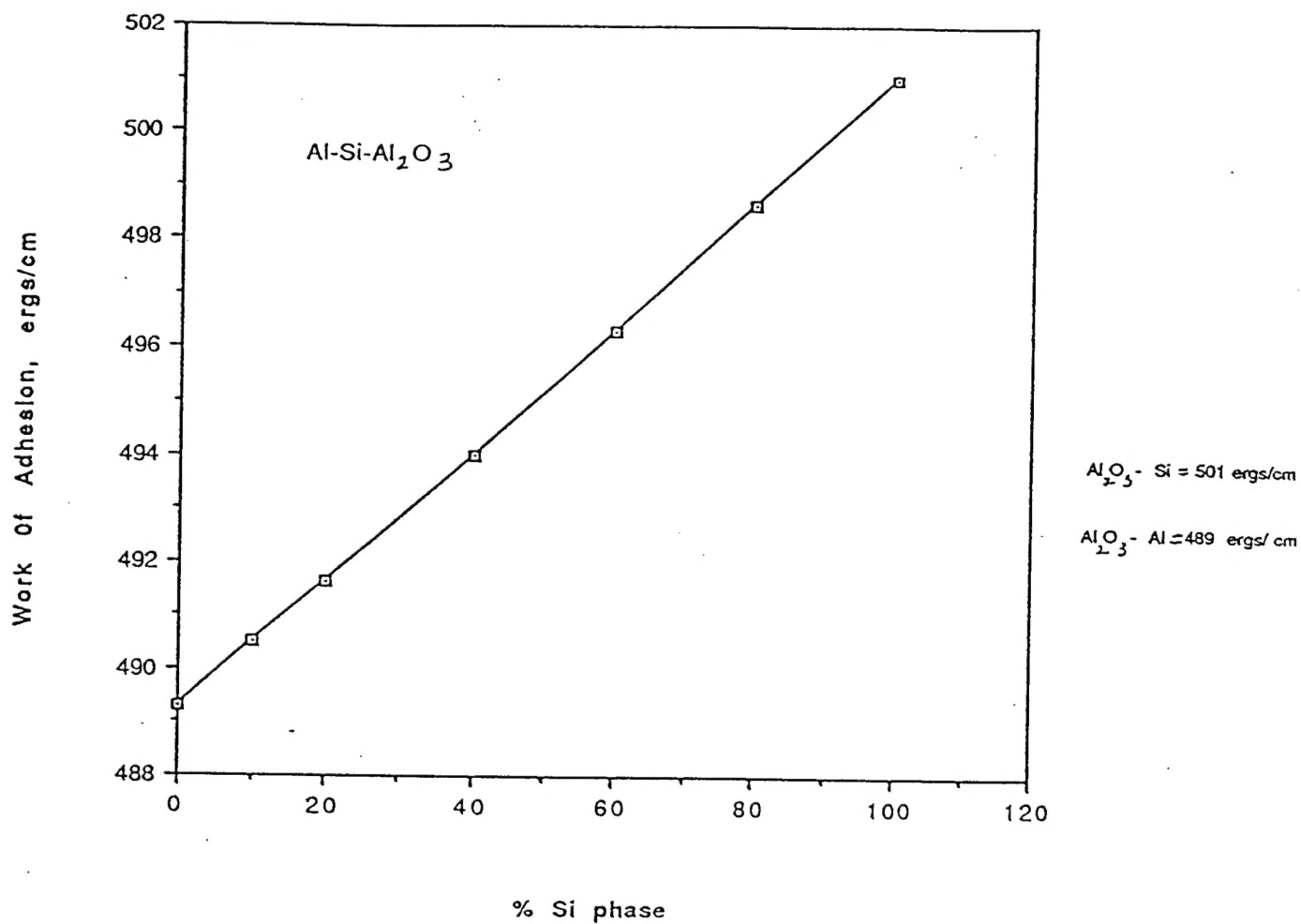


FIG 13. VARIATION IN WORK OF ADHESION WITH INCREASE IN VOLUME PERCENT OF SILICON PHASE AT THE INTERFACE